NOTE

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Spray pyrolyzed WO_x thin films

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Abstract : Thin films of WO_x have been prepared by simple and inexpensive spray pyrolysis technique. The films were prepared at different solution concentrations by keeping all other preparative parameters optimized. The effect of solution concentration on the formation of different phases of WO_x films is studied.

Keywords : Spray pyrolysis technique, tungsten oxide, X-ray diffraction

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Tungsten oxide (WO_3) is one of the transition metal oxides which has some interesting structural properties. Many investigations of WO_3 films have been carried out concerning practical electrochromic display devices and photoelectrochemical solar cells.

Since different forms of WO_3 films may be prepared by various methods [1–5], it is interesting to study the structural properties of WO_x films prepared by spray pyrolysis technique. In this technique, spray rate, substrate temperature, concentration of solution *etc* are the preparative parameters which affect semiconducting properties of the films. In particular for oxide films, oxygen deficient films are obtained due to non-optimization of the preparative parameters.

In this note, we report on the effect of solution concentration to be sprayed onto substrates, on the formation of different oxygen deficient phases of WO_x films prepared by spray pyrolysis technique. WO_x films were prepared by spraying ammonium tungstate solution onto glass substrates kept at 250°C and heat treated at 500°C in air for six hours. Solution concentration was varied between 0.01 *M* to 0.05 *M*. Thickness was varied from 0.28 μm to 2.2 μm. Films were lemon yellow in colour.

Structural identification of WO_x films was carried out using X-ray diffraction patterns of WO_x films prepared at various solution concentrations and are shown in Figure 1. It is found that the films were polycrystalline in nature. The '*d*' values were calculated only for the

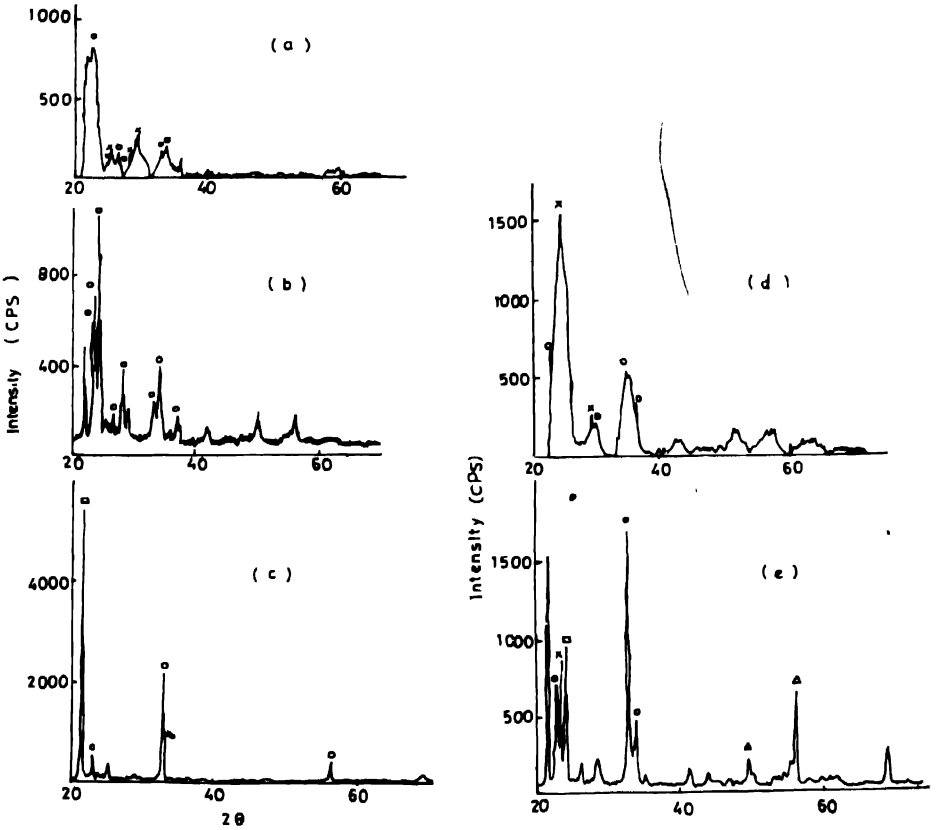

Figure 1. X-ray diffraction patterns for the films prepared with (a) 0.01, (b) 0.02, (c) 0.03, (d) 0.04 and (e) 0.05 *M*. solution concentrations.
• → $W_{20}O_{58}$, X → $W_{18}O_{49}$, O → WO_3T (triclinic); □ → $W_{25}O_{73}$, △ → WO_3

peaks with relative intensity (I/I_{max}) greater than 10%. The '*d*' values of planes were compared with standard '*d*' values taken from the ASTM diffraction data file, and different phase formations were identified. Close inspection of the X-ray patterns reveals that about five crystalline phases of WO_x *viz*., WO_3, WO_3T (triclinic), $W_{20}O_{58}$, $W_{18}O_{49}$ and $W_{25}O_{73}$ are observed. Different crystalline phases of WO_x films formed at various concentrations with relative intensities of the peaks are given in Table 1.

From the table it is clear that for 0.01 *M* solution concentration three phases are observed. Oxygen deficient phases ($W_{20}O_{58}$ and $W_{18}O_{49}$) consists of more than one peak. For 0.02 *M* solution concentration only single phase of WO_3T is observed. As solution

concentration increases above 0.02 *M*, oxygen deficient peaks increase, particularly for 0.05 *M*, five phases are observed (three oxygen deficient phases). This may be due to (i) incomplete decomposition of ammonium tungstate at deposition temperature of 250°C and (ii) insufficient time period for total conversion into WO_3 at 500°C.

Table 1. Formation of different crystalline phases of WO_x film with relative intensities of the peaks at various solution concentrations

Solution concentration *M*	Phases	I/I_{max} (%)
	$W_{20}O_{58}$	100, 18
0.01	$W_{18}O_{49}$	32, 16, 15
	WO_3T	24, 22, 16, 14
0.02	WO_3T	100, 63, 49
		40, 36, 23, 21 12
0.03	$W_{25}O_{73}$	100
	WO_3T	50, 20, 11
	$W_{18}O_{49}$	100, 24
0.04	WO_3T	39, 34, 16, 13
	$W_{20}O_{58}$	100, 26
	WO_3	49, 13
0.05	WO_3T	24
	$W_{25}O_{73}$	37
	$W_{18}O_{49}$	35

In conclusion, WO_x films prepared by spray pyrolysis technique are found to be solution concentration dependant. Single phase WO_3 films are obtained by optimizing solution concentration as 0.02 *M*.

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